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Integrated Thin Film Fluorescence NO_X Sensor: Concept

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Integrated Thin Film Fluorescence NO_x Sensor: Concept

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ABSTRACT

A fluorescence sensor system is proposed that integrates emission and detection methods, as well as optical and electronic components, in a thin film geometry. Predicted properties of this sensor include: increased sensitivity, shielding from unwanted radiation, wavelength filtering, potential operation at high temperatures, and miniaturization. The sensor can be tuned to measure a wide variety of species by varying its thin film corrugation periodicity. In particular, the sensor can be used to detect NO_x.

Keywords: fluorescence sensor, emission method, NO_x, grating, waveguide, surface plasmon

1 INTRODUCTION

The heightened awareness and regulation[1] of engine pollutants requires increasingly sensitive and sophisticated detection capabilities. Of particular interest to NASA is the detection of aircraft engine pollutants such as NO, NO_2 (NO_x). Such pollutants, along with CO, CO_2, and hydrocarbons, contribute to smog, ozone depletion, and acid rain. Unfortunately, the harsh environmental conditions in an aircraft engine produce logistical challenges that prevent adequate measurement of these pollutants. Therefore, a need exists for the development of a "next generation" of sensors capable of monitoring NO_x emissions from aircraft engines. Other potential applications include the detection of emissions from automobiles, heavy machinery, and power plants, as well as for biomedical applications.

Current NO_x sensor research and development is centered on either optical or electronic methods for detection. Electronic metal oxide thin film sensors have been developed which are miniature, sensitive, and offer economical/robust detection capability.[2–4] Such sensors typically operate by absorbing pollutants on the thin film surface. This absorption affects the chemical bonding in the film that, in turn, affects the film's electrical properties. For example, changing resistance or current flow in the oxide film can indicate the presence of a pollutant. Unfortunately, the absorption of different pollutants or non-pollutants may generate an identical electrical response in the oxide film. Thus, these devices lack adequate chemical selectivity.[5,6] In general, optical sensors exhibit better selectivity based upon the uniqueness of atomic absorption and emission lines,[7,8] however, they suffer from low signal to noise ratios.[9] Low power optical signals combined with high levels of optical background noise produce low signal to noise ratio signals that are difficult to detect. A fluorescence thin film sensor is proposed that retains the beneficial selectivity and miniature geometry characteristic of optical and electronic sensors, respectively, while improving the signal to noise ratio. The sensor also integrates a fluorescence emission method with an electronic detection method in a thin

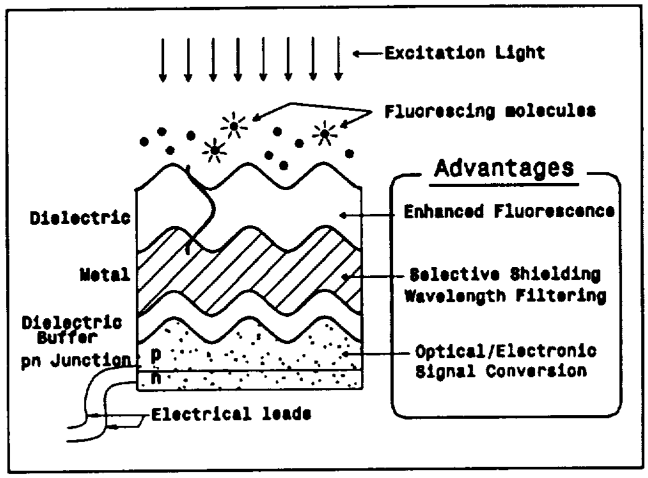

Figure 1: Integrated thin film sensor geometry.

film geometry.

The principles by which this sensor operates are described below. An experiment designed to validate and characterize the optical principles of the sensor is outlined. Furthermore, the test samples required and procedures utilized to fabricate these samples are described.

2 THEORY

The geometry of the proposed sensor is illustrated in Figure 1. The sensor consists of a stack of thin films adjacent to the species being detected; a solid, liquid or gas. The thin films comprising the sensor are, in order of increasing distance from the fluorescent material, a dielectric waveguide layer, a corrugated metal film, a dielectric buffer layer, and a sensing material layer. This geometry provides a radiative decay channel for the fluorescing molecules or atoms. This decay channel utilizes enhanced molecular fluorescence, surface plasmon cross coupling, and electron/hole pair production phenomena.

The decay channel opens when external radiation incident on the fluorescent material excites atoms/molecules into higher energy states. The incident radiation may also excite waveguide modes in the thin film stack. Since the fluorescent material is adjacent the thin film stack, intense electromagnetic fields from the guided modes overlap with and, hence, interact with the atoms in the fluorescent material. This interaction can cause an order of two magnitude enhancement in the fluorescence of molecules relative to that from molecules placed on a bare microscope slide.[10-13]

The excited molecules/atoms can decay and excite optical modes in the thin film stack. These modes include waveguide modes in the dielectric waveguide layer and surface plasmon modes confined to the dielectric waveguide/metal interface. The wavelength content of these modes is the same as that characterizing the fluorescence. Surface plasmon modes are lossy waveguide modes with electromagnetic field profiles peaked at the dielectric/metal interface. Surface plasmons are supported at opposite sides of the metal film in the proposed sensor. If the metal film is planar and thicker than the optical penetration depth (typically 50 nm), it is nearly opaque and radiative energy cannot be transmitted through it. Thus, surface plasmons on the side of the metal film opposite the fluorescing material cannot be excited by the fluorescence. However, the presence of a corrugation induces a "cross coupling" between surface plasmons supported at opposite sides of the metal film.[14-16] Surface plasmons supported at the metal/dielectric interface nearest the fluorescing molecules can excite surface plasmons in the same energy state on the opposite side of the metal film. For dissimilar dielectric media bounding the metal film, the cross coupling is restricted to a narrow range of wavelengths. This spectral transmission bandpass interval varies with both the corrugation periodicity and material choices. Thus, radiative energy within this small wavelength interval can be transmitted across an otherwise opaque metal film.

The presence of a corrugated thin metal film in the proposed sensor accomplishes several goals. First, it restricts the fluorescence radiative decay channel to a narrow wavelength interval. Only radiation within this wavelength interval is passed across the metal film. Secondly, it shields the detector from optical noise of unwanted sources. For high temperature environments, such as an aircraft engine, shielding from blackbody radiation is advantageous. A reduction in the noise combined with an enhanced signal results in an increased signal to noise ratio for the proposed sensor. Also, the presence of the corrugation allows several material property constraints to be relaxed. For example, to keep the transmission passband fixed at the desired detection wavelength, changes in the dielectric waveguide material can be compensated for by adjusting the corrugation periodicity. This property enables flexibility in material choice.

The electromagnetic field intensity of surface plasmon modes decreases exponentially with increasing distance from the supporting metal/dielectric interface. If the dielectric buffer layer thickness is small, the cross coupled surface plasmon fields penetrate across this barrier into the sensing material; likely a semiconductor pn junction. When this occurs, optical energy is absorbed into the sensing medium, affecting the electronic properties of this medium. Such effects can be detected electronically as changes in resistance, voltage, or current flow. Thus, the fluorescence optical energy is converted into electrical energy. Also, since the electronic detector is incorporated as a layer in the stack, the sensor can be miniaturized.

3 EXPERIMENTAL STRATEGY

The properties of the proposed sensor can be divided into optical and electronic components. The optical properties are based on the enhanced molecular fluorescence and surface plasmon cross coupling phenomena. Separately, enhanced molecular fluorescence[12] and surface plasmon cross coupling[15] phenomena have been experimentally verified. Evidence suggesting that both phenomena can be interrelated has been observed.[17] The goal of this experiment is to verify and characterize the combined effects of surface plasmon cross coupling and enhanced molecular fluorescence in thin film geometries suitable for NO_x detection.

The interaction of waveguide modes with molecules enhances the fluorescence from those molecules. Both the number and character of waveguide modes supported in a dielectric waveguide layer are dependent upon its thickness. Changing the layer thickness then affects the interaction between molecules and waveguide modes; i.e. the enhanced molecular fluorescence. Emission intensities of fluorescence radiation passed through the metal film via surface plasmon cross coupling should reflect these changes. Thus, by monitoring radiation intensities emitted from samples with different waveguide layer thicknesses, the combined effects of enhanced molecular fluorescence and surface plasmon cross coupling should be manifest and can then be characterized.

To do this, the sensor geometry is modified slightly as shown in Figure 2. This geometry consists of a fluorescent material layer, a dielectric waveguide layer, and a thin metal film. The fluorescent film layer consists of approximately 100 nm of photoresist spun on a fused silica (Corning 7059) microscope slide. A sinusoidal surface relief is then fabricated onto the photoresist layer. A waveguide layer of silicon nitride (Si_3N_4) is deposited on the corrugated photoresist layer. To form the final layer, silver (Ag) is deposited onto the waveguide layer. The corrugation is propagated throughout the thin film layers. Light transmitted through the sample and emitted into the air region is

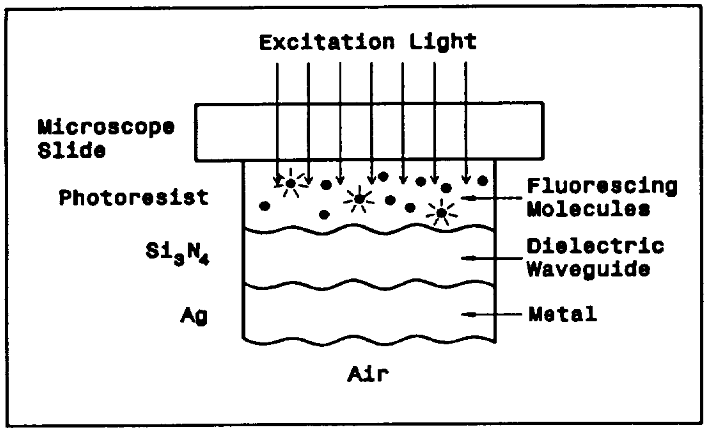

Figure 2: Sample geometry to test optical properties.

collected and analyzed for its wavelength and intensity content.

4 SAMPLE FABRICATION

A key feature in the thin film stack is the corrugation. The periodicity or pitch of this corrugation is determined by calculating the wavenumber "gap" between the surface plasmon dispersion curves at a desired fluorescence detection wavelength. Dispersion curves are graphical representations of the dispersion relation,

$$k_x = \frac{2\pi}{\lambda}\sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}, \tag{1}$$

where k_x is the wavenumber component parallel to the metal/dielectric interface, λ is the wavelength, ε_d and ε_m are the permittivity of the dielectric and metal, respectively. A metal film embedded in dissimilar dielectrics supports dissimilar surface plasmon modes at opposite sides of the metal film. As a result, surface plasmon states for an air/Ag/Si_3N_4 geometry are described by the two dispersion curves in the λ vs. k_x plot shown in Figure 3. A sinusoidal corrugation of period Λ boosts the wavenumber of a photonic state by an amount equal to the grating constant, $\frac{2\pi}{\Lambda}$. Thus, surface plasmon coupling occurs at the wavelengths where the momentum boost, $\frac{2\pi}{\Lambda}$, is equal to the separation between the dispersion curves, Δk_x. Due to scattering by irregularities on the metal surface, the surface plasmon dispersion curves have a finite width. Also, the dispersion curves in Figure 3 diverge for decreasing wavelength. Thus, only over a narrow range of wavelengths, centered at the desired fluorescence detection wavelength, is the momentum boost equal to the separation between the dispersion curves.

To fabricate the corrugation, photoresist is deposited on fused silica microscope slides using standard spin and soft bake techniques. The thickness of the photoresist layer is approximately 100 nm. The photoresist covered slides are then placed in a Lloyd's mirror arrangement, see Figure 4, for exposure by two interfering beams of Argon Ion laser light (λ = 458 nm). The microscope slides are index fluid matched to a glass prism with back sides covered with black tape to absorb stray light. The advantage of the Lloyd's mirror setup is twofold. First, the optical path difference of the two laser beams striking the photoresist is small which relaxes the coherence length requirement of the laser. Secondly, both beams strike the photoresist at an angle θ relative to the surface normal. The grating

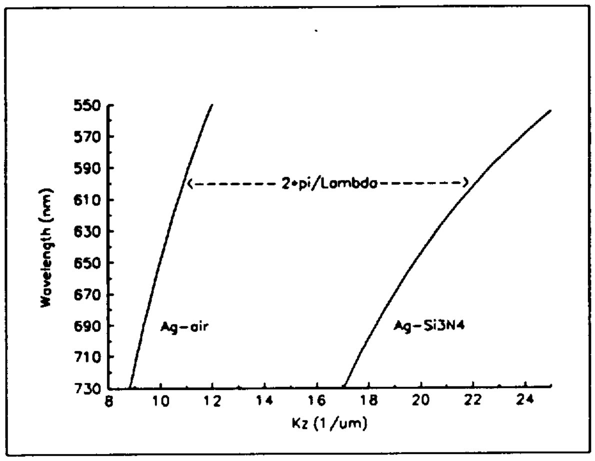

Figure 3: Wavelength vs. wavenumber.

periodicity, Λ, and θ are related by

$$\sin\theta = \frac{\lambda_o}{2\Lambda}, \tag{2}$$

where λ_o denotes the wavelength of the exposure light. By placing the Lloyd's mirror setup on a rotation stage, the desired periodicity can be "dialed in" with a simple rotation of the entire mirror and prism assembly. Gratings with submicron periodicity are fabricated in this manner.

After exposure, the photoresist is developed and hard baked. Using RF sputtering deposition, a silicon nitride (Si_3N_4) waveguide layer and a silver (Ag) film layer are deposited on the corrugated photoresist surface. The Ag layer surface relief, of approximate thickness equal to 100 nm, replicates the underlying sinusoidal corrugation.

5 EXPERIMENTAL SETUP

To test the optical properties of the proposed sensor, the modified samples are placed on a rotation stage. This stage is located in front of a condenser lens pair as shown in Figure 5. To excite the fluorescence, laser light is delivered to the sample via a multimode optical fiber. To maintain light at a constant angle of incidence during sample rotation, the fiber is attached to the rotation stage. Light transmitted through the silver film and emitted from the irradiated spot on the sample is then collected, in part, by the condenser lens pair. The condenser lens pair images the light onto the entrance slit of the spectrometer. Light passed by the spectrometer is detected by a cooled photomultiplier tube (PMT). Voltage pulses generated by the PMT are analyzed with a Stanford Research SR400 photon counter. This equipment provides the wavelength and intensity analysis required to evaluate both the cross coupling and enhanced molecular fluorescence phenomena occurring in the sample. A block diagram of the data acquisition equipment is shown in Figure 6.

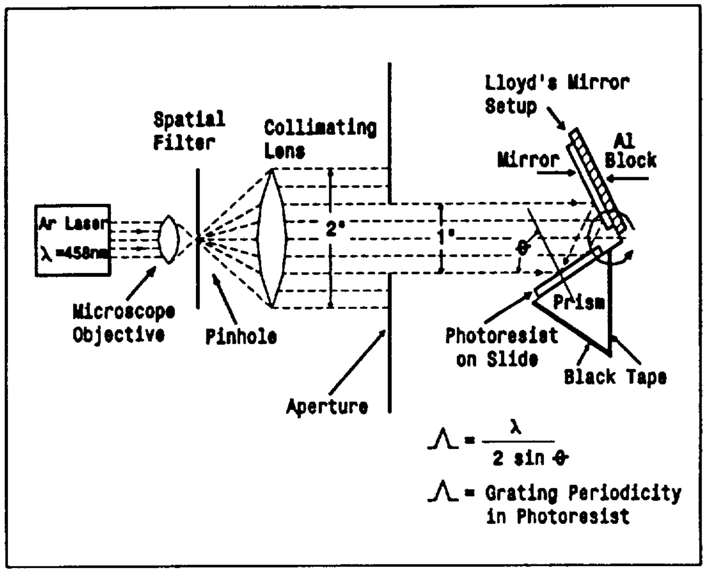

Figure 4: Holographic grating fabrication system.

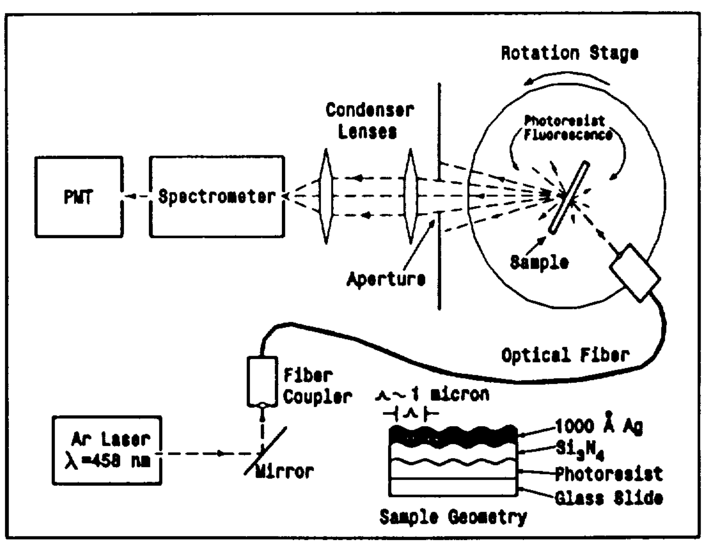

Figure 5: Fluorescence data acquisition setup.

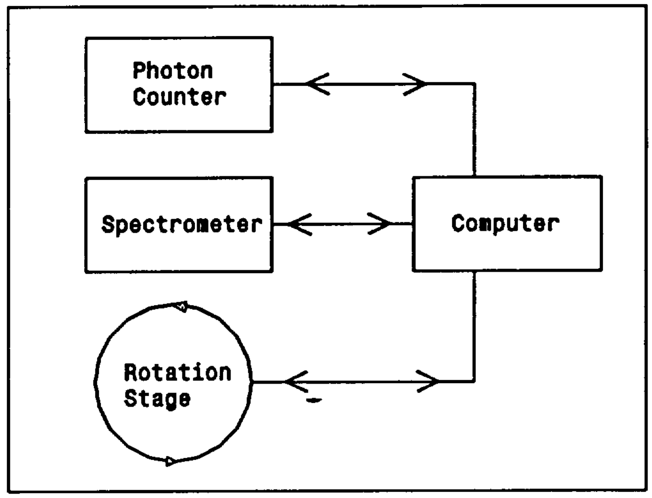

Figure 6: Block diagram of data acquisition equipment.

6 CONCLUSIONS

An integrated thin film fluorescence NO_x sensor concept and method of verifying the optical properties of the concept are proposed. Although designed for NO_x detection, the sensor can be tailored to other applications. The concept combines the properties of enhanced molecular fluorescence, surface plasmon cross coupling, and electrical detection. Enhanced molecular fluorescence can increase the fluorescence signal to be detected by several orders of magnitude. Surface plasmon cross coupling: (1) filters the wavelength content of fluorescence being detected, (2) shields the detector from unwanted radiation sources, and (3) when combined with fluorescence enhancement, increases the signal to noise ratio. Conversion of an optical signal into an electrical signal is achieved by integrating a semiconductor film into the sensor thin film stack. This integration enables miniaturization of the sensor. The resulting sensor combines the optimum properties of current optical and electronic sensors: the selectivity and sensitivity of optical detectors, and the robust and compact nature of electronic sensors. Future work will include the use of SiC substrates for high temperature applications.

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